

THEORY OF INITIATION OF EXPLOSION IN SOLIDS
BY AN INTENSE LIGHT FLASH

By

T. BODDINGTON

Laboratory for the Physics and Chemistry of Solids,
Cavendish Laboratory,

CAMBRIDGE.

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The evolution of the temperature profile within a solid capable of exothermic decomposition is derived from an approximate analytic solution of the equation describing heat conduction in the presence of continuously distributed heat sources due to chemical decomposition and to the absorption of an intense, short duration pulse of light. The critical light intensity capable of giving rise to a thermal explosion is deduced and a minimum, critical intensity is shown to exist. The model predicts all the major experimental features of ignition by light.

Several sensitive explosives having high absorption coefficients for light in or near the visible range have been ignited by intense light flashes of short duration¹⁻⁴. The future development of such sources may lead to light sources capable of igniting a wider range of explosives.

It is known that many methods of igniting explosives depend on the initial formation of a localized region of high temperature - hot spot¹. The use of an intense light source of short duration

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offers the possibility of introducing controlled hot spots into an explosive and thus of gaining some knowledge of the high temperature decomposition kinetics of the explosive. Blanchard^{5,6} has described the initial results of a digital computer study of the relevant thermal regime and the present author⁷ has used an approximate analytic model to explain Barchtold's results⁴ for silver nitride. Since no generally applicable model of the ignition process has been described, and in view of the usual limitations of numerical solutions even an approximate analytic solution would be useful. In general the thermal regime is extremely complex. Accordingly several simplifying approximations are made in this paper for the sake of mathematical tractability but they have reasonable physical validity and result in little error in the critical ignition intensities.

BASIC EQUATION

For simplicity the following one-dimensional regime is considered. Light is incident normally and uniformly on the free surface of a homogeneous, isotropic explosive mass filling the half-space $z > 0$. The free surface is in contact with a vacuum and the entire explosive mass is initially at the uniform temperature T_0 . The equation expressing local conservation of energy has the form

$$\sigma C \frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial z^2} + q \sigma \nu \exp(-E/RT) + \int \alpha E_0 e^{-\alpha z} dz \quad (1)$$

where the symbols have the following meanings:

T - absolute temperature, σ - density, c - heat capacity,
 t - time, k - thermal conductivity, q - exothermicity of the
 explosive decomposition (energy/unit mass), ν - frequency factor,
 E - activation energy, α - absorption coefficient, λ - wavelength
 of light, E_0^λ - light energy flux density in the interval $(\lambda, \lambda + d\lambda)$
 at $z = +0$, differing from the incident value by a reflexion
 component.

In general both E_0^λ and α are complicated functions of
 wavelength, so that an analytic solution of (1) is impossible in
 the case of polychromatic radiation. If monochromatic radiation
 of integrated intensity E_0 (energy/unit area/unit time) at $z = +0$
 is used, the relevant equation

$$\sigma c \frac{\partial T}{\partial t} = \underbrace{k \frac{\partial^2 T}{\partial z^2}}_{\text{I}} + \underbrace{q \sigma \nu \exp(-E/RT)}_{\text{II}} + \underbrace{\alpha E_0 e^{-\alpha z}}_{\text{IV}} \quad (2)$$

is more tractable. The use of (2) as the basic equation
 implies that Arrhenius kinetics and exponential absorption
 adequately describe the regime. It is further assumed that all
 the quantities involved, with the exception of T and E_0 are
 independent of z and t . Latent heats of phase transformation,
 reactant consumption and hydrodynamic effects are ignored.

The boundary condition at $z = 0$ which satisfies Stefan's
 radiation law makes a solution difficult. The Newtonian boundary
 condition.

$$\frac{1}{T - T_0} \frac{\partial T}{\partial z} = \text{const.}, \quad z = 0 \quad (3)$$

will be used below.

If the light is switched on at the time $t = 0$ the initial conditions are

$$T = T_0, E_0 = 0 \quad \text{when} \quad t < 0 \quad (4)$$

INERT PHASE

Equation (2) with conditions (3) and (4) remains extremely intractable but since term III of (2) is small compared with the other terms until explosion is imminent it may be neglected in the first stage of the solution. (2) can now be written in the form

$$\frac{\partial U}{\partial \tau} = \frac{\partial^2 U}{\partial \rho^2} + A e^{-\rho} \quad (5)$$

where $\tau = \kappa t \alpha^2 / \sigma c$, $\rho = \xi \alpha$ are a dimensionless time and distance respectively; $A = f(\tau) = E_0 / \kappa \alpha$ is a temperature proportional to the energy flux and $U = T - T_0$. Equations (3) and (4) become

$$\left(\frac{\partial U}{\partial \rho} \right)_{\rho=0} = h U_{\rho=0}; \quad h = \text{const.}, \quad (6)$$

$$U = 0, \quad f(\tau) = 0 \quad \text{when} \quad \tau < 0. \quad (7)$$

The Laplace transform of (5) is

$$\frac{d^2 u}{d\rho^2} - pu = - \int_0^\infty e^{-\rho} f(\tau) e^{-p\tau} d\tau = e^{-\rho} \bar{f}(p) \quad (8)$$

say, because of (7), where $u = \int_0^\infty U e^{-p\tau} d\tau$.

The Laplace transform of (6) is

$$\frac{du}{dp} = hu \quad \text{at} \quad p = 0 \quad (9)$$

The general solution of (8) is

$$-u = \frac{e^p \bar{f}(p)}{1-p} + B e^{sp} + C e^{-sp}; \quad B, C = \text{const.}, \quad s^2 = p.$$

B must be zero for admissible (finite) solutions and (9) gives

$$C = -(1+h) \frac{\bar{f}(p)}{(1-p)(s+h)}$$

so, finally, the solution of (5) is given by

$$U = e^{-p} \mathcal{L}^{-1} \left\{ \frac{\bar{f}(p)}{p-1} \right\} - (1+h) \mathcal{L}^{-1} \left\{ \frac{\bar{f}(p) e^{-sp}}{(p-1)(s+h)} \right\} \quad (10)$$

where the operator \mathcal{L}^{-1} corresponds to the Laplace inverse transformation.

If the "emission function", $f(\tau)$, of the light source is specified, (10) can be put in explicit form by standard methods⁸.

For brevity only the step function

$$\left. \begin{aligned} f(\tau) &= 0, & \tau < 0 \\ f(\tau) &= A_0, & \tau > 0 \end{aligned} \right\} \bar{f}(p) = A_0 p^{-1}$$

corresponding to a constant flux source with zero rise time, will

be considered here. (10) now has the form

$$\begin{aligned} \frac{U}{A_0} &= e^{-p} (e^{-1}) + \frac{h+1}{h} \left[\text{erfc}(c/2x) - e^{hp+h^2x} \text{erfc}(c/2x + hx) \right] \\ &\quad - (h+1) \left\{ \frac{1}{2} e^{\frac{c^2}{2}} \left[\frac{e^{-p}}{h+1} \text{erfc}(c/2x - x) + \frac{e^p}{h-1} \text{erfc}(c/2x + x) \right] - \frac{h}{h^2-1} e^{hp+h^2x} \text{erfc}(c/2x + hx) \right\} \end{aligned} \quad (11)$$

where $x = \tau^{\frac{1}{2}}$ and $\operatorname{erfc} z = 1 - \operatorname{erf} z = \frac{2}{\sqrt{\pi}} \int_z^{\infty} e^{-\xi^2} d\xi$.

It is shown in appendix I that if $\tau \lesssim 10^2$ then (11) can be written in the approximate form

$$\begin{aligned} \frac{U}{A_0} = & 2x i \operatorname{erfc}(c/2x) - e^{-c} + \frac{1}{2} e^{\tau+c} \operatorname{erfc}(x+c/2x) + \frac{1}{2} e^{\tau-c} \operatorname{erfc}(x-c/2x) \\ & + h \left\{ 2x i \operatorname{erfc}(c/2x) + e^{\tau+c} \operatorname{erfc}(x+c/2x) - \operatorname{erfc}(c/2x) - 4x^2 i^2 \operatorname{erfc}(c/2x) \right\} \\ & + O(h^2) \end{aligned} \quad (12)$$

where $i^n \operatorname{erfc} z = \int_z^{\infty} i^{n-1} \operatorname{erfc} \xi d\xi$; $i^0 \operatorname{erfc} z = \operatorname{erfc} z$

The form of the repeated integrals of the error function complement and related functions is shown in Fig.1.

If $h=0$, (12) has the form

$$\frac{U}{A_0} = 2x i \operatorname{erfc}(c/2x) - e^{-c} + \frac{1}{2} e^{\tau+c} \operatorname{erfc}(x+c/2x) + \frac{1}{2} e^{\tau-c} \operatorname{erfc}(x-c/2x), \quad (13)$$

a solution previously given by Carslaw and Jaeger⁸.

Now in cases of interest $h \lesssim 10^{-2}$ (see Appendix E) so (13) can be used as a good approximation to (12). Hence (13) is a good description of the evolution of the temperature profile provided that chemical reaction is insignificant. It will not be valid if high efficiency photochemical processes can occur.

INERT DECAY OF HOT SPOT

The total energy dissipated per unit area when the light has been switched on for a time t_0 is given by

$$\mathcal{E} = E_0 t_0 = \int_0^{\infty} c U dz \quad \text{and thus}$$

$$\int_0^{\infty} U dz = \frac{\mathcal{E}}{\sigma_c} = A_0 x_0^2 = \widetilde{T}, \quad \text{say}$$

where $x_0^2 = \tau_0 = k t_0 x^2 / \sigma_c$.

The temperature profile given by a light pulse of fixed integrated energy density, \mathcal{E} and of dimensionless duration α_0^2 is given by

$$U/\tilde{T} = U/A_0 \alpha_0^2 \quad (14)$$

where U/A_0 is given by (13) and \tilde{T} is constant.

The profiles given by (14) are plotted in Fig. 2.

If the light source is switched off at a time t_0 the appropriate emission function is

$$\begin{aligned} f(\tau) &= A_0 [1 - H(\tau - \tau_0)] \quad , \quad \tau > 0 \\ f(\tau) &= 0 \quad , \quad \tau < 0 \\ \bar{f}(p) &= A_0 p^{-1} (1 - e^{-p\tau_0}) \quad , \end{aligned} \quad (15)$$

where H is the Heaviside function.

The combination of (10) and (15) with $h = 0$ gives

$$U = U_*(\tau) - U_*(\tau - \tau_0) \quad (16)$$

where $U_*(\tau)$ is given by equations (7) and (13). (16) describes

the entire inert regime corresponding to a rectangular light flash.

An interesting limiting case occurs when A_0 tends to infinity while τ_0 tends to zero in such a way that the total energy (which is proportional to $A_0 \tau_0$) remains constant.

The appropriate emission function is

$$f(\tau) = \frac{\mathcal{E}\alpha}{\sigma c} \delta(\tau, 0) ; \quad \bar{f}(p) = \tilde{T}$$

and gives the profile

$$\frac{U}{\hat{T}} = \frac{1}{2} e^{-\rho^2/4\tau} \left[Z_0(x - \rho/2\tau) + Z_0(x + \rho/2\tau) \right]$$

from (10) where $Z_0(z) = e^{z^2} \operatorname{erfc} z$. (17) is the limiting form of (16) as $\tau_0 \rightarrow 0$, $\mathcal{E}^0 = \text{const.}$, and with $\tau = 0$ yields the limiting case of (13): $U = \hat{T} e^{-\rho}$, a result entirely to be expected for the initial temperature distribution produced by a light pulse of infinitesimal duration.

REACTIVE PHASE

In the above treatment heat evolution due to chemical reaction has been entirely ignored. In this section the effect of chemical reaction is introduced as a perturbation of the inert evolution of the temperature profile, in the following way. Firstly, chemical reaction during the time for which the light is switched on is ignored and, secondly, the rate of decay of the hot spot due to heat conduction after the light source is switched off is considered to be identical to that of the inert case. The validity of this procedure is examined in appendix II. Although not entirely justifiable this procedure is of the utmost importance in simplifying the subsequent analysis.

If chemical reaction is ignored prior to the time τ_0 then the inert temperature decay after the time τ_0 is given by (16).

In particular

$$(U/A_0)_{\rho=0} = \frac{2}{\sqrt{\pi}}(x-x') + Z_0(x) - Z_0(x')$$

where

$$\tau' = \tau - \tau_0, \quad x' = \sqrt{\tau - \tau_0} = \sqrt{\tau'} \\ \text{Hence } \frac{1}{A_0} \left(\frac{\partial U}{\partial \tau} \right)_{\rho=0} = Z_0(\sqrt{\tau' + \tau_0}) - Z_0(\sqrt{\tau'}) \quad (18)$$

in the inert case.

Now, by definition, term IV of (2) is zero for $\tau > \tau_0$, $\tau' > 0$ so Frank-Kamenetskii's exponential approximation^{9,24} can be used to write (2) in the dimensionless form

$$\frac{\partial \theta}{\partial \tau} = \frac{\partial^2 \theta}{\partial \rho^2} + \delta e^{\theta}$$

or approximately

$$\frac{\partial \theta}{\partial \tau} \approx \frac{\partial^2 \theta}{\partial \rho^2} \Big|_{\text{inert}} + \delta e^{\theta} \quad (19)$$

$$\text{where } \theta = \frac{E}{RT_s^2} (T - T_s), \quad \delta = \frac{q_0 \nu E}{\alpha^2 k R T_s^2} \exp(-E/RT_s)$$

$$\text{and } T_s = T_0 + U(c=0, \tau=\tau_0) \quad (20)$$

In the $\frac{1}{\lambda}$ approximations the Arrhenius rate expression is expanded about the highest temperature produced in the inert phase of regime, where the effect of chemical reaction is most important. The necessary condition for a thermal explosion to occur in an explosive with zero order kinetics is that the temperature somewhere tend to infinity. In the present regime the temperature is greatest at the origin, $\rho=0$. Only the evolution of the temperature at the free surface will be further considered.

Since

$$\left. \frac{\partial \theta}{\partial \rho^2} \right|_{\text{inert}} = \left. \frac{\partial \theta}{\partial \tau} \right|_{\text{inert}} = \frac{E}{R T_s^2} \left. \frac{\partial U}{\partial \tau} \right|_{\text{inert}} \quad \text{for } \tau > \tau_0.$$

(18) and (19) may be combined to give

$$\frac{d\theta}{d\tau} = B g(\tau, \tau_0) + \delta e^{\theta} \quad \text{for } \theta = 0 \quad (21)$$

where

$$B = \frac{E A_0}{R T_s^2}, \quad g(\tau, \tau_0) = Z_0(\sqrt{\tau + \tau_0}) - Z_0(\sqrt{\tau})$$

and, for convenience, the prime on τ' has been dropped. The ordinary differential equation (21) can be integrated to give

$$\eta \exp \left[B \int_{\tau_0}^{\tau} g d\tau \right] = - \int \exp \left[B \int_{\tau_0}^{\tau} g d\tau \right] d\tau + \text{const} \quad (22)$$

where $\eta = e^{-\theta}$.

It is clear that explicit explosion conditions cannot be derived from (22) unless $g(\tau, \tau_0)$ has a simple form. Fortunately $g(\tau, \tau_0)$ has simple asymptotic forms at both small and large values of τ_0 . These two extremes will be considered separately.

SHORT DURATION FLASH

If $\tau_0 \ll 1$ then

$$\begin{aligned} g(\tau, \tau_0) &= Z_0(\sqrt{\tau + \tau_0}) - Z_0(\sqrt{\tau}) \approx \tau_0 \frac{dZ_0(x)}{dx} \\ &= \left[Z_0(x) - \frac{x^{-1}}{\sqrt{\pi}} \right] \tau_0 \approx - \frac{\tau_0}{\sqrt{\pi}} x^{-1}, \end{aligned}$$

if $x \ll 1$.

Hence $B \int_{\tau_0}^{\tau} g d\tau \approx \frac{2}{\sqrt{\pi}} B \tau_0^2 \tau^{\frac{1}{2}}$ and (22) with the initial condition, $\theta = 0$ when $\tau = 0$, gives

$$\eta = \mu(1+y) + (1-\mu)e^y \quad (23)$$

where

$$y = \left\{ \frac{2}{\sqrt{\pi}} \cdot \frac{EA_0 x_0}{RT_s^2} \right\} \tau^{\frac{1}{2}}, \quad \mu = \frac{\pi}{2} \cdot \frac{q\sigma\gamma R}{\kappa\alpha^2 E} \left(\frac{T_s}{T} \right)^2 \exp(-E/RT_s)$$

Fig. 3 shows the nature of (23) for various values of the parameter μ . Clearly the condition for explosion to occur is $\mu > 1$.

LONG DURATION FLASH

If $\tau_0 \gtrsim 1$, $\tau \ll 1$ then

$$\begin{aligned} q(\tau, \tau_0) &= Z_0(\sqrt{\tau_0 + \tau}) - Z_0(\sqrt{\tau}) \\ &\simeq Z_0(\sqrt{\tau_0}) + \tau \left[Z_0'(\sqrt{\tau_0}) - \frac{1}{\sqrt{\pi\tau_0}} \right] - \left[\frac{2}{\sqrt{\pi}} \tau + \tau^2 \right] \\ &\simeq Z_0(x_0) - 1 \end{aligned}$$

Hence $B \int_0^\tau q dt \simeq - \frac{E\hat{T}}{RT_s^2} \frac{1 - Z_0(x_0)}{\tau_0} \tau$ and (22) with the appropriate initial condition gives

$$\eta = \varepsilon + (1-\varepsilon)e^{C\tau} \quad (24)$$

where $C = \frac{E\hat{T}}{RT_s^2} \frac{1 - Z_0(x_0)}{\tau_0}$

and $\varepsilon = \frac{\delta}{C} = \frac{q\sigma\gamma\tau_0 \exp(-E/RT_s)}{\alpha^2 \kappa \hat{T} [1 - Z_0(x_0)]}$

Fig. 4 shows the nature of (24) for various values of the parameter ε . Clearly the condition for explosion to occur is $\varepsilon > 1$.

CONDITION FOR EXPLOSION

The conditions for explosion are given by

$$\mu > 1 \quad (\tau_0 \ll 1)$$

$$\varepsilon > 1 \quad (\tau_0 \gtrsim 1)$$

Although critical energy densities, \mathcal{E}_{cr} , could be computed from these criteria, it is preferable to find an explicit formula for $\mathcal{E}_{cr}(\tau_0)$ even at the expense of some accuracy. Consequently a simple approximation to T_s is required. By definition

$$T_s - T_0 = U(\rho=0, \tau'=0) = A_0 \left\{ \frac{2x_0}{\sqrt{\pi}} + Z_0(x_0) - 1 \right\}$$

from (13). Or since $A_0 \tau_0 = \tilde{T}$,

$$T_s - T_0 = \tilde{T} \Phi^{-1}(x_0)$$

$$\text{where} \quad \Phi(x) = x^2 \left\{ \frac{2x}{\sqrt{\pi}} + Z_0(x) - 1 \right\}^{-1}$$

It can be shown that if x is small

$$\Phi(x) = 1 + \frac{4x}{3\sqrt{\pi}} + \frac{1}{3} \left[\frac{16}{3\pi} - 1 \right] x^2 + \dots$$

$$= 1 + 0.752x + 0.233x^2 + O(x^3)$$

and if x is large

$$\Phi(x) = \frac{\sqrt{\pi}x}{2} \left[1 + \frac{\sqrt{\pi}}{2x} + \frac{1}{2} \left(\frac{\pi}{2} - 1 \right) \frac{1}{x^2} + \dots \right]$$

$$= 0.786 + 0.885x \left[1 + \frac{0.286}{x^2} - \frac{0.190}{x^3} + O(x^{-4}) \right]$$

Fig. 5 shows a plot of $\Phi(x)$ and its linear asymptotes. It is

clear that $1 + \frac{\sqrt{\pi}}{2}x = 1 + 0.885x$ estimates $\Phi(x)$

for all $x \geq 0$ with an error of less than 5%.

The critical condition for a short duration flash, $\mu = 1$, may be written in the form

$$\frac{1}{a_0^2 x^2} \exp(-E/RT_0) \left[\Phi^{-1}(x_0) + \frac{T_0}{\hat{T}} \right] = 1$$

where $a_0^2 = \frac{2}{\pi} \left(\frac{T_R}{T_A} \right) \left(\frac{D}{\gamma} \right)$ is constant for a given explosive

and $T_R = E/R$, $T_R = q/c$; $D = k/\sigma c$ is the thermal diffusivity. Since $\Phi^{-1}(x) \simeq -\frac{4x}{3\sqrt{\pi}}$ for small x and $T_0/\hat{T} \leq 0.3$ in cases of interest, the critical condition is given approximately

by

$$\frac{\hat{T}}{T_A} = K_0 \Phi(x_0)$$

where $K_0 = \left[\ln \left(\frac{1}{a_0^2 x^2} \right) \right]^{-1} - \frac{T_0}{T_R}$.

The critical condition for the long duration flash, $\xi = 1$, has the form

$$\frac{\hat{T}}{T_A} = \Phi(x_0) \left\{ \left[\ln \frac{2x_0 T_R / \pi (1 - Z_0(x_0))}{\hat{T} a_0^2 x^2} \right]^{-1} - \frac{T_0}{T_A} \right\} = K \Phi(x_0), \text{ say.}$$

This expression does not yield \hat{T} explicitly, but since T_0/T_R is small ($\sim 10^{-2}$) and $a_0^2 x^2 \sim 10^{-12}$ for the conventional explosives, K is insensitive to large variations in the argument of the logarithm.

Thus $\hat{T}/T_A \simeq K_0 \Phi(x_0)$ and

$$K \simeq \left[\ln \frac{2x_0 / \sqrt{\pi} (1 - Z_0(x_0))}{a_0^2 x^2} \right]^{-1} - \frac{T_0}{T_A} \quad (25)$$

Since $Z_0(x) \simeq 1 - \frac{2}{\sqrt{\pi}} x$ when x is small, (25) gives the correct limiting value K_0 as x_0 tends to zero.

Thus the critical condition for explosion has the approximate form

$\tilde{T}/T_A = K \Xi$ where K is given by (25) and is a feebly decreasing function of α_0 , while Ξ increases strongly with α_0 according to the approximate formula

$$\Xi = 1 + 0.885 \alpha_0$$

Ignoring the variation in K the critical condition is

$$\tilde{T} = K_0 \Xi T_A \quad (26)$$

This formula should predict critical energy densities with a maximum error of 10% if $\alpha_0 \ll 1$ or $1 \lesssim \alpha_0 \lesssim 10$. It will further be assumed that (26) remains a good approximation for the intermediate range of α_0 where a solution of (21) is difficult. According to (26) the critical energy density is given by

$$C_c = K_0 \left(\frac{\sigma c T_A}{\alpha} \right) \left[1 + \frac{\Xi}{2} \alpha_0 \right] = K_0 \left(\frac{\sigma c T_A}{\alpha} \right) \left[1 + \sqrt{\frac{\pi D}{4}} \cdot \alpha t_0^{\frac{1}{2}} \right] \quad (27)$$

DISCUSSION

In the derivation of critical energy densities for ignition numerous assumptions and approximations have been introduced, the validity of which requires examination before a comparison between (27) and experimental measurements is attempted.

1. CONSTANCY OF PARAMETERS.

For real explosives there are two sources of variation of the relevant thermochemical parameters. Temperatures occurring in

the ignition regime range between 300°K and on 2000°K so that significant variations, particularly in the activation energy¹⁰, are to be expected. The error introduced in this way can be minimized by selecting averaged values for the density and heat capacity and the high temperature values for the activation energy and K_0 .

It is shown below that variable composition due to reactant consumption has only a small effect on the parameters.

2. LATENT HEAT EFFECTS

If a zone of thickness $\rho_m \alpha^{-1}$ must be melted before the critical temperature profile becomes established then an extra amount of energy $\Delta \tilde{E}$ must be expended, where

$$\Delta \tilde{E} \approx \rho_m \alpha^{-1} L \quad (\text{or } \Delta \tilde{T} = \frac{L}{c} \rho_m)$$

and L is the latent heat. Thus

$$\frac{\Delta \tilde{E}}{\tilde{E}_c} = \frac{\Delta \tilde{T}}{T_c} = \frac{\rho_m}{K_0 \alpha} \cdot \frac{L}{c T_A} \approx \frac{L}{c T_A} \frac{\ln[U_3/(T_m - T_0)]}{K_0 \alpha}$$

where T_m is the melting point of the explosive. Since (L/c) is about 100°K for both organic and inorganic explosives, the latter ratio may be as small as 10% for a sensitive explosive with a high melting point (e.g. AgH_3) or as large as unity for an insensitive explosive with a low melting point (eg. TNT). The value of \tilde{E}_c given by (27) is of the correct order of magnitude but for a more accurate estimate the amount $\sigma L \alpha^{-1} \ln[U_3/(T_m - T_0)]$ should be added.

3. REACTANT CONSUMPTION

It can be shown that if α_0 is small the fraction of undecomposed explosive ξ satisfies the condition

$$-\ln \xi < \frac{\alpha_0^2}{\frac{\pi}{2} + \frac{\sqrt{\pi}}{2} \alpha_0} \left(\frac{-t_0}{\theta_R} \right) \exp \left\{ -t_0 \frac{\sqrt{\pi} \alpha_0}{2} \right\} \quad \text{if } t < 1$$

in the neighbourhood of critical conditions, where $\theta_0 = E(T_0 - T_S)/RT_S^2$

and $\theta_R = ET_R/RT_S^2$. In cases of interest $-\theta_0/\theta_R \lesssim 0.5$ and

$\theta_0 \simeq -10$ so that $\xi > 0.8$ throughout the explosive "induction period"¹², $t < 1$, provided that $\alpha_0 \lesssim 0.2$. Exact numerical solutions⁶ show that reactant consumption remains of little importance for times rather larger than $\alpha_0 = 0.2$. The small amount of reactant consumption during the "induction period" justifies the neglect of hydrodynamic effects.

4. DELAY TIME TO EXPLOSION

If τ_0 is small the reduced time, τ_* , required for the surface temperature to become infinite is given by

$$\mu(1+y_*) + (1-\mu)e^{y_*} = 0$$

from (23). If the regime is critical, $\mu = 1$ and τ_* becomes infinite.

If, however, the regime is slightly supercritical, $\mu \geq 1.1$, this author¹¹ has shown that $1 < \tau_*/\tau_\infty < 9$, where $\tau_\infty = \delta^{-1}$ is

the reduced adiabatic explosion time at the temperature T_S ,

so that for temperatures which are only slightly supercritical the delay time to explosion is of the same order of magnitude as the adiabatic explosion time at the surface temperature.

Thus in the immediate neighbourhood of critical^a conditions

$$\tau_* \approx 10\tau_\infty \approx 10(\theta_0)_{cr}^{-2} \approx 10K_0^2$$

and since K is typically $\sim 10^{-1}$ for the conventional explosives

$$\tau_* \lesssim 10^{-1}.$$

Hence the assumption that $\lambda \ll 1$ made in the derivation of (23) is reasonably valid.

Similarly if τ_0 is large (24) gives $\tau_*/\tau_\infty = \epsilon \ln \frac{\epsilon}{\epsilon-1}$, so that if $\epsilon = 1.1$, $\tau_*/\tau_\infty = 2.6$. The delay time near critical conditions is given by

$$\tau_* \approx 3\tau_\infty \approx 3(B)_{cr}^{-1} \approx 3K^2 \left(\frac{T_A}{T_R} \right) \tau_0$$

and, since $\frac{T_A}{T_R} \sim 5$ for the conventional explosives, $\tau_* \approx \tau_0 / 6$

Hence the assumption that $\lambda \ll 1$ does not remain valid throughout the explosive induction period unless $\tau_0 \lesssim 1$.

5. DEPARTURE FROM EXPERIMENTAL CONFIGURATION

Actual experiments on ignition by light are carried out using a light flash with a non-rectangular emission function focussed on a finite area of an explosive slab of finite thickness. The conditions under which the results for the present idealized configuration remain valid in practice must be considered.

It can be seen from Fig.2 that the light flash causes significant heating only in a thin surface layer of thickness $ca. \lambda^{-1}$ (corresponding to $\rho = 1$). In fact, it can be shown from (13)

that the reduced distance to the inflexion in the temperature profile, ρ_i , is given by

$$\rho_i \approx \ln \sqrt{\pi} = 0.572 \quad \text{if} \quad x_0 \ll 1$$

$$\rho_i \approx \ln(\sqrt{\pi} x_c) \quad \text{if} \quad x_c \gg 1$$

and that if ρ/x is large the temperature excess U decays as $e^{-\rho}$.

If the rear surface of the explosive slab corresponds to $\rho > 4$ the light is attenuated by a factor greater than $e^4 \approx 50$, so a slab thicker than $4\alpha^{-1}$ reflects negligible radiation from its rear surface. In addition heat losses from the rear surface into a vacuum or a solid substrate are small provided that $\tau_0 \lesssim 10$, i.e. $\rho_i < 3$.

Consequently the idealized analysis remains applicable if the thickness of the explosive slab exceeds $10\alpha^{-1}$, say. These considerations are in good agreement with Borchtold's observations⁴ that the critical ignition energy of an Ag_3N film deposited on glass is sensibly constant if the film thickness exceeds 0.5μ when $\alpha^{-1} \approx 10^{-5}$ cm.

In most cases of interest $\alpha^{-1} < 10^{-2}$ cm and thus the idealized treatment is applicable to any explosive mass thicker than 1 mm.

If a parallel beam of light is incident normally upon a semi-infinite cylinder of finite diameter d , the lateral heat

is negligible compared with the heat loss from the surface $\dot{q} = 0$ provided that $d \gg \alpha^{-1}$. Since this free surface heat loss has been shown to be negligible the idealized results remain good approximations as long as $d \gg 1$.

If a condenser system is used, so that some radiation is no longer incident normally on the free surface, the radiation is degraded into thermal energy closer to the surface $(r=0)$ than in the case of normal incidence. The effect on the maximum surface temperature attained is small and the effective width of the heated zone is reduced by less than 30% even when the semi-angle of the light cone, ω , is as great as 45° . Ignoring reflexion effects, it can be shown that E_{cr} is equal to the value given by (27) multiplied by a factor not less than $\cos \omega$. In ^{fact} the reflexion effects, which have been avoided in defining E_0 and related quantities, should make the experimental quantity (critical source energy reaching explosive) / (surface area illuminated) insensitive to the type of condenser system used.

The remarks of this section apply only if no lateral heat sinks in the form of inert confinement or unilluminated explosive are present strongly to modify the predicted temperature evolution.

6. REAL LIGHT SOURCES

The output of a real light source is in general so complicated a function of time that the present approach becomes unproductive. If, however, the flash duration, t_0 , is considerably less than $(D \times 2)^{-1}$, so that $\alpha_0 \ll 1$, then the shape of the emission function is unimportant. To demonstrate this fact, h is

equated to zero in (10) which can then be written in the form

$$U = \frac{1}{2} [f(\tau)] * \left[e^{-\rho^2/4x^2} \{ Z_0(x + \rho/2x) + Z_0(x - \rho/2x) \} \right], \quad (28)$$

$$\text{where } [f_1(\tau)] * [f_2(\tau)] = \int_0^\tau f_1(\tau') f_2(\tau - \tau') d\tau'$$

is the convolution of f_1 and f_2 .

If x_0 is small it can be shown from (28) that the temperature distribution for $x = x_0$ satisfies the inequalities

$$e^{-\rho^2/4x_0^2} \int_0^{\tau_0} f(\tau) d\tau < U < e^{-\rho^2/4(1+\tau_0)^2} \int_0^{\tau_0} f(\tau) d\tau \quad \text{for } \rho \gtrsim x$$

$$\int_0^{\tau_0} f(\tau) d\tau > U > (1 - \frac{2x_0}{\sqrt{\pi}}) \int_0^{\tau_0} f(\tau) d\tau \quad \text{for } \rho = 0$$

These inequalities show that if $\tau_0 \ll 1$ the initial temperature distribution and, therefore, the critical energy density for explosion are virtually independent of τ_0 and depend only upon the quantity $\int_0^{\tau_0} f(\tau) d\tau$ which is proportional to the integrated energy output of the light source. Although the present treatment requires that α is constant, it should remain valid for polychromatic light such that $\frac{\Delta\alpha}{\alpha} \ll 1$. This condition is satisfied by many explosives¹ in the visible region but unfortunately α is, in general, so small for visible light that existing sources are several orders of magnitude too feeble to give rise to explosion.

Clearly the general case of ignition by polychromatic

light could only be described by numerical methods.

It is concluded that the present idealized model, subject to the reservations of the above discussion, corresponds closely to reported experimental configurations¹⁻⁴,

It is difficult to estimate the effect of the mathematical approximations used in the above analysis upon the critical values of the parameters μ and ε but it is unlikely that they are in error by a factor as large as 5. Since E_c varies as the logarithm of μ_c or ε_c the consequent error in E_c is not greater than 10% for explosives with activation energies greater than 20 Kcal.mole⁻¹. A further error, not greater than 10% provided that $\tau_0 \lesssim 10$, is incurred by using the simplified formula (27) instead of the exact explosion criteria. Certainly, (27) should estimate critical energy densities to within one order of magnitude.

COMPARISON WITH EXPERIMENT

Equation (27) gives a good approximation to the critical energy density for ignition provided that the duration of the light flash does not exceed a standard conduction time $t_c = (D\alpha)^{-1}$ by more than about one order of magnitude. The criterion becomes inaccurate for long duration flashes. The thermal diffusivity of most explosives lies in the range 10^{-3} - 10^{-4} cm²sec⁻¹, while the absorption coefficient in cases of interest ranges from 10^2 to 10^5 cm⁻¹. Thus the standard conduction time t_c may range from 0.1 μ sec (at large α) to 1 sec (small α). The value of

t_c is most important in determining the way in which the critical energy varies with flash duration.

EFFECT OF FLASH DURATION

If the conditions of an experimental determination of \mathcal{E}_c as a function of t_c are such that $t_0 \gg t_c$ then (27) predicts

$$\mathcal{E}_c = K_0 \sigma_c T_A \sqrt{\frac{\pi}{4} D} \left[t_0^{\frac{1}{2}} + \sqrt{\frac{t_c}{\pi}} \cdot t_c^{\frac{1}{2}} \right] \approx K_0 \sigma_c T_A \sqrt{\frac{\pi}{4} D} \cdot t_0^{\frac{1}{2}} \quad (28)$$

In this case the critical energy varies linearly with (and is almost proportional to) the square root of the flash duration. It is interesting to note that if the feeble variation of K_0 with α is ignored (28) predicts that the critical energy density

$$\mathcal{E}_c \approx \sqrt{\frac{\pi}{4} K_0 \sigma_c} \cdot T_A K_0 t_0^{\frac{1}{2}} \quad (29)$$

is independent of the absorption coefficient. This fact suggests that (29) may remain valid for polychromatic light satisfying the condition, $t_0 \gg t_c$ or $\alpha^2 \gg (Dt_0)^{-1}$. Berchtold^{1,4} has ignited Berthollot's "explosive silver", Ag_3N , with polychromatic light for which $\alpha \gtrsim 10^4 \text{ cm}^{-1}$ using flashes of millisecond duration. Thus in this case the condition $t_0 \gg t_c$ can be satisfied if $D \gg 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$. Although $D(Ag_3N)$

not been measured, it is reasonable to assume that the latter condition is satisfied. Fig.6 shows the variation of \mathcal{E}_c with the square root of the flash duration calculated from Berchtold's data⁴. It can be seen that the variation is almost linear. Moreover Berchtold reports that, allowing for experimental error, the critical energy is independent of the range of wavelengths of the light used. This fact supports the tentative suggestion made above concerning "long" duration flashes of polychromatic radiation (see appendix III).

With the opposite extreme of a "short" duration flash the predicted behaviour is quite different. If $\alpha^2 t_0 D \ll 1$, (27) can be written in the form

$$\mathcal{E}_c = K_0 \frac{\sigma c T_A}{\alpha} \left[1 + \sqrt{\frac{\pi t_0}{4 t_c}} \right] \approx K_0 \sigma c T_A / \alpha$$

Thus the critical energy of a short flash should be almost independent of the flash duration and inversely proportional to the absorption coefficient (ignoring the variation of K_0 with α). Unfortunately suitable "short" flash duration experiments have not yet been performed since the presently available light sources cannot deliver adequate power within a bandwidth for which α is both sensibly constant and sufficiently large. (A giant-pulse "laser" system operating in the presently available power range but with a resonant wavelength of 2-3000 Å would constitute a suitable radiation source). However it has been observed experimentally¹ that the critical ignition energy of a short

duration flash increases strongly as the effective mean absorption coefficient of the spectral range employed is increased.

An extremely important conclusion to be drawn from (27) is that as the flash duration tends to zero the critical energy density tends to the finite value

$$E_{min} = \frac{\sigma c T_R}{\alpha} \left\{ \left[\ln \left(\frac{1}{\alpha_0^2 \alpha^2} \right) \right]^{-1} - \frac{T_0}{T_R} \right\} \quad (30)$$

which is the minimum energy density, at the wavelength corresponding to α , that is capable of giving rise to explosion."

EFFECT OF AMBIENT TEMPERATURE

If E_{cr} is measured for a series of values of T_0 using a light source of constant duration then according to (27)

$$\frac{\partial E_{cr}}{\partial T_0} = - \frac{\sigma c}{\alpha} \bar{\Phi}(\alpha_0) = \text{const.} \quad (31)$$

provided that the variation of the thermochemical parameters over the relevant temperature range is negligible. Moreover $\partial E_{cr} / \partial T_0$ will remain sensibly constant even if large variations in α_0 (such that $\alpha_0 \ll 1$) are permitted. The linear variation of E_{cr} with T_0 predicted by (31) will only be valid as long as T_0 is considerably less than the "explosion temperature" of the system explosive plus environment. The applicability of the foregoing analysis depends not only upon the fact that E/RT_0 is large

but also upon the assumption that the system is inherently stable in the neighbourhood of the temperature T_0 . However, a truly adiabatic explosive mass necessarily explodes if it is initially at any temperature greater than absolute zero. A real explosive mass is stabilized below a certain temperature T_{cr} by its finite rate of heat loss to the environment and above that temperature either decomposes quietly^{12,13} or explosively^{9,14,15} according to the nature of its reaction kinetics. The range of ambient temperature for which the present analysis is applicable cannot be uniquely stated since T_{cr} depends upon the environment and is not, therefore, a characteristic parameter of the explosive. The explosion criteria derived here are valid if the reaction rate of the system is negligible at the ambient temperature.

If \tilde{C}_{cr} is plotted against T_0 the low temperature linear asymptote of the resultant curve intercepts the temperature axis at

$$T_i = T_A \left[\ln \left(\frac{1}{a_0^2 \alpha^2} \right) \right]^{-1},$$

a value independent of flash duration.

A number of explosives have been shown to obey the linear law predicted by (31). Fig.7 illustrates the results obtained by McKuslan¹⁶ for lead styphnate. A linear law is clearly a satisfactory description of the results over a wide temperature range. The value of T_i is approximately 750°K. Similar results have

been obtained with the following explosives for which the values of T_i are given in brackets : AgNO_3 (555°K)¹⁷, PbN_6 (655°K)⁴, NH_3NI_3 , "nitrogen iodide" (355°K)¹⁸, $\text{AgNO}_3 \cdot \text{Ag}_2\text{C}_2$ (ca 800°K)⁴. It is important to note that, for a given wavelength, $T_i(\lambda)$, unlike T_{cr} , is an eigen-property of the explosive. The reported approximate equality of T_i and T_{cr} ^{1,4} is to be regarded as fortuitous. From the definitions of T_i and T_s

$$T_s - T_o = (K/K_o) (T_i - T_o)$$

under critical conditions. Hence if κ_o is small ($K/K_o \approx 1$), $T_s \approx T_i$ and T_i is approximately the minimum surface temperature that must be produced by a short duration flash in order to cause an explosion. As a further illustration of the significance of T_i it is noted that (26) may be written in the form

$$\frac{\epsilon_\alpha \alpha}{\sigma c} = \tilde{T}_\alpha = \Phi(T_i - T_o) \quad (32)$$

For a short duration flash ϵ_α is the amount of energy required to raise unit area of a surface "skin" of thickness α^{-1} to the temperature T_i .

ORDERS OF MAGNITUDE

The above treatment has been concerned with the quantity ϵ^{+o} whereas the experimentally important quantity is ϵ^{-o} , the incident energy density outside the explosive. These two variables are related by the formulas¹⁹

$$\frac{\sigma}{c} = \frac{1}{t_\lambda} \epsilon^{-\sigma}, \quad \frac{1}{t_\lambda} = \frac{4\pi}{(n+1)^2 + K_o^2}, \quad K_o = \frac{\alpha \lambda}{4\pi}$$

where n is the refractive index and K_o the absorption index.

Now for the organic explosives, $n \sim 1.5 - 1.6$, and for the inorganic explosives¹, $n \sim 2 - 5$, and $\alpha \lesssim 10^5 \text{ cm}^{-1}$ so that $\frac{1}{t_\lambda}$ is greater than 90% except in the neighbourhood of a strong absorption edge ($\alpha \sim 10^5 \text{ cm}^{-1}$) where it may fall to ca 50%. Thus in discussing orders of magnitude it is reasonable to equate t_λ to unity.

Table 1 gives the values for some common explosives of the thermochemical parameters needed to calculate E_{cr} from (27). It is noteworthy that both cT_h and D are almost constant at the values 10^4 cal.cm^{-3} and $10^{-3} \text{ cm}^2 \text{ sec}^{-1}$, respectively, in spite of the large variation of explosive character among the substances considered. Since $a_o \lesssim 10^{-9} \text{ cm}$, $\alpha \lesssim 10^5 \text{ cm}^{-1}$ and $T_o/T_h \simeq 1.5 \times 10^{-2}$

$$K_o = \left[\ln \left(\frac{1}{a_o^2 \alpha^2} \right) \right]^{-1} - \frac{T_o}{T_h} \lesssim 4 \cdot 10^{-2}$$

Hence the critical energy densities for short duration flashes are of the order of

$$\frac{4 \cdot 10^2}{\alpha} \text{ cal.cm}^{-2} \simeq \frac{10^3}{\alpha} \text{ J.cm}^{-2},$$

(where α is expressed in cm^{-1}) whether the explosive be primary or secondary. Most of the experimental workers have not reported the absolute magnitude of E_{cr} but some quantity

considered to be proportional to it (such as the square of the voltage on a storage condenser). Consequently a detailed numerical comparison of the present theory and experimental results cannot be made. However, Courtney-Pratt and Rogers^{1,22} have reported absolute data for AgN_3 using radiation in the near ultraviolet for which $\alpha = 10^3 - 10^4 \text{ cm}^{-1}$, $\tau_0 \approx 0.15$. They find $E_{cr} \approx 8 \times 10^{-2} \text{ cal cm}^{-2}$. This value is yielded by (27) and Table 1 if $\alpha = 1.39 \times 10^3 \text{ cm}^{-1}$, and by (32) with the experimental result $T_1 = 555^\circ\text{K}$ if $\alpha = 1.63 \times 10^3 \text{ cm}^{-1}$.

Both these values of the absorption coefficient lie within the range corresponding to the wavelength range employed. Berchtold^{4,1} has also estimated that E_{cr} is of the order of 1 joule cm^{-2} for a large number of substances. The relevant values of α are not reported, but the present theory requires them to have the reasonable magnitude of ca 10^3 cm^{-1} . Clearly the present theory predicts the correct magnitude of the critical energy density.

The value of E_{cr} given by (27) could be extremely low for a well designed light pulse. For instance, in the neighbourhood of the fundamental absorption edge the absorption coefficient may be as great as 10^5 cm^{-1} so that the critical energy density for the corresponding radiation is about $10^{-2} \text{ joule cm}^{-2}$, if the flash duration is less than $0.1 \mu\text{s}$. Clearly a high absorption coefficient makes the most efficient use of the incident radiation. If α is large an incident intensity of about $10^3 \alpha^{-1} \text{ joule cm}^{-2}$ delivered

in less than $10^2 \alpha^{-2}$ seconds will suffice to initiate the conventional explosives (α is in units of cm^{-1}). This requires a source power in excess of $10 \alpha \text{ watt. cm.}^{-2}$, say one Megawatt cm.^{-2} near an absorption edge. (The ruby laser system of McClung and Hellworth²³ can operate at this power for ca $0.2 \mu\text{s}$ at a wavelength of 6943 \AA). Because most explosives have very low absorption coefficients for radiation in the visible range (10^{-1} to 10 cm^{-1}), existing sources cannot deliver the adequate critical intensities in this part of the spectrum alone. Consequently, with the exception of some coloured "exotic" substances, e.g. Ag_3N^4 , initiation is caused by the ultraviolet radiation accompanying the ineffective "light" flash. The apparently dissimilar "sensitivities" of primary and secondary explosives must be ascribed in the main to the fortuitous positioning of their absorption edges with respect to the energy distribution of existing high intensity, short duration flashes. For example a xenon flash tube has a number of sharp lines between 5000 and 12,000 \AA and, more importantly, a fairly flat continuous background with a 20% power range of 2,400 - 22,000 \AA . Moreover, cut-off is rapid beyond these limits, being complete on the short wavelength side at ca 2000 \AA . The secondary class consists mostly of organic substances whose crystals possess molecular lattices . PETN, a typical member of this class, transmits well down to 3000 \AA . Its absorption coefficient rises to 10^3 - 10^4 cm^{-1} at 2000 \AA . The primary class consists of such ionic materials as AgN_3 for which absorption sets in at 3850 \AA . α becomes ca 10^3 cm^{-1} at 3000 \AA rising

approximately to $ca 10^5 \text{ cm}^{-2}$. Consequently a xenon flash which is critical for AgH_3 would be subcritical for PETN by nearly two orders of magnitude even if the two explosives had identical thermochemistry.

NUMERICAL SOLUTIONS

Blanchard ^{5,6} and Bouchon ⁶ have described computer solutions of the finite difference equations corresponding to the flash initiation of an explosive with first order kinetics. The relevant values of x_c lie in the range from 10^{-3} to 30 and the general form of the solutions agrees well with the present theory. One important difference emerges. Critical conditions can be found numerically only by trial and error - a process costly in computer time. The majority of the computed results are presented in terms of "useful energy", \mathcal{E}_u , computed as the product of flux density, E_0 , and the time taken for explosion to occur. This procedure corresponds to a situation in which light continues to illuminate the explosive for some time after a critical temperature profile has been established owing to the existence of an apparent explosive induction time. It is shown in appendix II that for a flash of constant intensity and zero rise time

$$\mathcal{E}_u / \mathcal{E}_c \simeq 1 + \frac{\tau_{\infty}}{\tau_0} \ln(1 + \tau^{-1})$$

where τ_{∞} is defined in section 4 and τ is given by

$$\Gamma = \tau_0 \left(1 + \frac{\sqrt{\pi}}{2} z_0 \right)^{-1}.$$

When τ_0 is large, $\Gamma/(1+\Gamma) \simeq 1$ and $E_u \simeq E_c$, but when τ_0 is small $E_u/E_c \simeq 1 + \frac{\tau_0}{K} \ln(1 + K\tau_0^{-1})$. Since E_c is finite at $\tau_0 = 0$, E_u tends to infinity as τ_0 tends to zero.

E_u is a poor approximation to the critical energy density for very short flashes.

This result is in agreement with Moerkhamp's experiments¹⁸ on nitrogen iodide in which $E_u t_0$ was found to be roughly constant. This particular form $E_u \propto t_0^{-1}$ was conditional by the shape of the light flash employed and is of no special significance.

CONCLUSIONS

The present model of flash initiation, which takes only thermal effects into account, satisfactorily describes all the major experimental features of the process. This supports experimental evidence^{1, 2, 4, 16, 22} that initiation by light is essentially a thermal regime. In the case of the conventional explosives the sensitivity towards initiation by light is affected very little by thermochemistry but strongly by the magnitudes of the absorption coefficient and flash duration.

The agreement between the present model and experiment suggests that the conditions necessary for the occurrence of a thermal explosion are also sufficient to engender a macroscopic explosion or a transition to a stable detonation regime, although further experimental work on secondary explosives may show that

and is not universally true.

The model should assist the design of flash ignition experiments and enable useful combinations of thermochemical parameters to be extracted from their results.

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APPENDIX I : EFFECT OF HEAT TRANSFER AT FREE SURFACE

The boundary condition at $z=0$ which satisfies Stefan's law for black body radiation has the form

$$\kappa \frac{\partial T}{\partial z} = \sigma_s [(T_c + U_c)^4 - T_c^4],$$

where $\sigma_s = 5.67 \times 10^{-5} \text{ erg cm}^{-2} \text{ sec}^{-1} \text{ K}^{-4}$ is Stefan's constant

This may be written in the form

$$\left(\frac{\partial T}{\partial z} \right)_{z=0} = \frac{\sigma_s}{\kappa \alpha} [(T_c + U_c)^4 - T_c^4] = h U_c$$

according to (6). Hence the maximum value of h is

$$h_{\max} \approx \frac{\sigma_s U_c^3}{\kappa \alpha}, \text{ since } U_c \lesssim 2000^\circ \text{C.}$$

Adopting the representative value $\kappa = 5 \times 10^4 \text{ erg cm}^{-1} \text{ sec}^{-1} \text{ K}^{-1}$,

it is found that $h_{\max} < 10 \alpha^{-1}$ where α is in units of cm^{-1} .

Now $\alpha^{-1} \lesssim 10^{-3} \text{ cm}$ in cases of interest so that $h_{\max} < 10^{-2}$ and

$h \ll h_{\max}$ for most of the regime.

If $h \neq 0$ the surface temperature is slightly lower than that given by (13). It can be shown that the fractional reduction in the excess surface temperature (U) is $ca \ hx$, which is always small provided that $\tau_c < 10^2$.

It can further be shown that the reduced distance between the surface and temperature maximum given by (12) is approximately hx at all times. Thus in cases of interest the maximum temperature occurs at a point extremely close to the free surface and (13) is a good approximation to (11).

APPENDIX II EFFECT OF CHEMICAL REACTION

Heat evolution due to chemical reaction will remain small during the illumination if the flash duration is much less than the isothermal half life of the explosive at the maximum temperature produced by the light flash i.e. if

$$\gamma t_0 \exp(-E/RT_0) \ll 1$$

Conventional explosives satisfy this condition if $t_0 \lesssim 10^{-6}$ sec.

A reasonable estimate of the effect of chemical reaction can be obtained by finding the extent of reaction in an explosive constrained to follow the inert temperature evolution of the free surface as given by (13). The rate equation for a first order reaction is

$$\frac{d\xi}{dt} = -\xi \gamma \exp(-E/RT)$$

where ξ is the fraction of explosive undecomposed. Since $\xi = 1$ when $t = 0$, this can be written in the form

$$-\ln \xi = \gamma \int_0^{t_0} \exp(-E/RT) dt$$

where $T(t)$ is to be derived from (13).

The integral can be evaluated approximately by using the Frank-Kamenetski expansion⁹ about the maximum inert temperature, T_0 , where the contribution to the integral is most important²⁴.

This procedure yields

$$\begin{aligned} -\ln \xi &= (\theta_0 \tau_\infty)^{-1} \int_0^{\tau_0} e^\theta d\tau \\ &< \frac{2\tau_0^2}{\theta_0^2 \theta_\lambda^2 \tau_\infty} [e^{\theta_0} - \theta_0 - 1] \end{aligned}$$

since $-\theta \leq -\theta_0 \left(1 - \frac{x}{x_0}\right)$.

Hence $-\ln \xi \lesssim \frac{-2x_0^2}{\theta_0 \theta_R \tau_\infty}$,

since $\theta_0 \lesssim -10$ in cases of interest.

The ratio of the temperature increase due to reaction in the absence of conduction and the increase due to the absorption of radiation is given by

$$R = \theta_R(1-\xi)/-\theta_0 \lesssim -\frac{\theta_R}{\theta_0} \left[1 - \exp\left\{-\frac{2\tau_0}{\theta_0 \theta_R \tau_\infty}\right\}\right] \quad (\text{II.1})$$

If $\tau_0 \ll 1$ then $R \lesssim \frac{S}{\theta_0^2} \cdot 2\tau_0$. For a critical heating regime

$\frac{S}{\theta_0^2} = \frac{2}{\pi}$ since $\mu = 1$. Hence

$$R_{cr} \lesssim \frac{4}{\pi} \tau_0$$

and heating due to chemical reaction is negligible while the light is switched on if $\tau_0 \lesssim 0.1$ say.

If $1 < \tau_0 \ll \theta_R^2 \approx 10^2$ the condition $\varepsilon = 1$ gives $R_{cr} = \frac{2x_0}{-\theta_0}$

so R remains small if $x_0 \lesssim 1$. The neglect of chemical reaction prior to the time t_0 is therefore justified for a critical flash if $t_0 \lesssim t_0^*$.

During the reactive phase of the regime the rate at which the surface temperature falls owing to conduction differs from that of the inert case but an argument similar to that of

Rideal and Robertson²⁵ suggests that the effect is small. Throughout the induction period^{9,24}, $\theta < 1$, with which this treatment is exclusively concerned, the temperature increase due to reaction remains less than T_g^2/T_A while the total temperature drop across the hot spot is initially $T_g - T_0$. In all cases of interest the ratio of these two quantities, $|\theta_0|$, is greater than 10 because of the high activation temperatures T_A involved. Consequently until the end of the induction period is reached the perturbation of the temperature profile caused by chemical reaction is small and the use of (19) is reasonable.

Blanchard^{5,6} and Bouchon⁶ have shown that if an extremely intense flash is used the effect of conduction is negligible and if the light source remains on after a critical profile has been established no abrupt change of $\partial v / \partial t$ is observed. The development of the free surface temperature of such a regime obeys the equation

$$\frac{dv}{d\tau} = B + \delta e^{\theta}, \quad (II.2)$$

$$\theta = \theta_0 \text{ when } \tau = 0,$$

where $B = \frac{A_0 E}{RT_g^2}$ represents the heating due to the light alone.

The solution of (II.2) is given by

$$\eta = -\frac{\delta}{B} + \left(\eta_0 + \frac{\delta}{B}\right)e^{-B\tau}, \quad (II.3)$$

where $\eta_0 = e^{-\theta_0}$.

The variation of $\theta - \theta_0$ with τ given by (II.3) is shown in Fig. 8. The reduced time required to produce a critical temperature profile ($\dot{t} = 0$) is given by $\exp(\bar{B}\tau|_{\dot{t}=0}) = \eta_0(1 + \delta/B\eta_0)/(1 + \delta/B)$ and the reduced time taken to reach infinite temperature is given by

$$\exp(\bar{B}\tau|_{\dot{t}=\infty}) = (1 + \delta/B\eta_0) / (\delta/B\eta_0)$$

Hence the "useful energy" of Blanchard and Bouchon is related to the critical energy by the expression

$$\begin{aligned} E_u/E_{cr} &= 1 + (\tau|_{\dot{t}=\infty} - \tau|_{\dot{t}=0}) / \tau|_{\dot{t}=0} \\ &= 1 + \frac{\tau_\infty}{\tau_0} \frac{\delta}{B} \ln(1 + B/\delta) \end{aligned}$$

where δ corresponds to critical conditions.

Since the value of (δ/B) or from (26) is approximately $\tau_0/K\Phi(x_0)$, E_u becomes considerably greater than E_{cr} if $\tau_0 \ll K_0^{-1}$.

Appendix III.

Polychromatic radiation.

It is possible to obtain good approximate solutions of the present problem provided that certain restrictions are imposed on the relevant range of α . The reasoning closely follows that of the foregoing analysis and the expressions involved are cumbersome. Consequently only an outline of the procedure and the major results will be given below.

The quasi-inert initial phase of the monochromatic regime is governed by the equation

$$\sigma c \frac{\partial U}{\partial t} = \kappa \frac{\partial^2 U}{\partial z^2} + \alpha E_0 e^{-\alpha z} \quad (\text{III},1)$$

with the conditions

$$\frac{\partial U}{\partial z} = 0, \quad z = 0, \quad t > 0 \quad (\text{III},2)$$

$$U = 0, \quad E_0 = 0, \quad t < 0 \quad (\text{III},3)$$

and since this system is linear its solutions, U , are additive. Although the general solution is awkward the solutions of interest for the case of a rectangular light pulse are relatively simple. In particular, from (13)

$$U_s = \frac{t_0}{\sigma c} \int \alpha E_0 \bar{\Phi}^{-1}(x_0) d\lambda, \quad (\text{III},4)$$

where the integral is to be taken over the entire emission range of the light source. The cases of "long" and "short" duration flashes will be considered separately.

Short flash. If $\alpha^2 \ll (Dt_0)^{-1}$ then

$$\bar{\epsilon}^{-1}(x_0) \approx 1 - \frac{4x_0}{3\sqrt{\pi}} \quad \text{and (III,4) gives}$$

$$U_s = \frac{t_0}{\sigma c} \int \alpha E_0^\lambda d\lambda \cdot \left[1 - \frac{4}{3\sqrt{\pi}} \sqrt{\frac{k t_0 \hat{\alpha}^2}{\sigma c}} \right]$$

where $\hat{\alpha} = \int \alpha^2 E_0^\lambda d\lambda / \int \alpha E_0^\lambda d\lambda$ is an average

absorption coefficient. (It is assumed that the light has a constant colour, $E_0^\lambda = E_1(\lambda) \cdot E_2(t)$, so that $\hat{\alpha}$ is constant). The inert decay given by combining solutions like (18) is

$$\sigma c \frac{dU}{dt} = -t_0 \sqrt{\frac{k}{\pi \sigma c}} \int \alpha^2 E_0^\lambda d\lambda \cdot t^{-\frac{1}{2}}, \quad \beta = 0,$$

where time is measured from t_0 . Hence the analogue of (21) is

$$\begin{aligned} \frac{d\theta}{dt} = & - \frac{E t_0}{\sigma c R T_s^2} \sqrt{\frac{k}{\pi \sigma c}} \int \alpha^2 E_0^\lambda d\lambda \cdot t^{-\frac{1}{2}} \\ & + \frac{q \nu E}{c R T_s^2} \exp(-E/R T_s) e^\theta \end{aligned}$$

which with the initial condition $\theta = 0$ when $t = 0$ has the solution (cf.(23))

0

$$\eta = M(1+\gamma) + (1-M)e^\gamma \quad (\text{III}, 6)$$

where

$$\gamma = \frac{2Et_0}{\sigma_c RT_s^2} \sqrt{\frac{k}{\pi \sigma_c}} \int \alpha^2 E_0^\lambda d\lambda \cdot t^{\frac{1}{2}}$$

and

$$M = \frac{\pi}{2} \cdot \frac{q RT_s^2 \exp(-E/RT_s) \cdot \nu (\sigma_c)^3}{k t_0^2 c E \left\{ \int \alpha^2 E_0^\lambda d\lambda \right\}^2}.$$

Clearly the condition for explosion is $M > 1$ or, rearranging and using (III,5) the critical condition is

$$\begin{aligned} \frac{t_0}{\sigma_c T_A} \int \alpha E_0^\lambda d\lambda &= \frac{1}{\sigma_c T_A} \int \alpha \mathcal{E}^\lambda d\lambda = \frac{\bar{\alpha}}{\sigma_c T_A} \int \mathcal{E}^\lambda d\lambda \\ &\simeq \left[1 + \frac{4}{3\sqrt{\pi}} \sqrt{\frac{k t_0 \hat{\alpha}^2}{\sigma_c}} \right] \left[\left\{ \ln \left(\frac{1}{\alpha_0^2 \hat{\alpha}^2} \right) \right\}^{-1} - \frac{T_0}{T_A} \right], \end{aligned}$$

where $\bar{\alpha} = \int \alpha E_0^\lambda d\lambda / \int E_0^\lambda d\lambda$.

The critical energy is given by

$$\mathcal{E}_c = \int \mathcal{E}^\lambda d\lambda = \frac{\sigma_c T_A}{\bar{\alpha}} \left[1 + \frac{4}{3\sqrt{\pi}} \sqrt{\frac{k t_0 \hat{\alpha}^2}{\sigma_c}} \right] \left[\left\{ \ln \left(\frac{1}{\alpha_0^2 \hat{\alpha}^2} \right) \right\}^{-1} - \frac{T_0}{T_A} \right]$$

which should be compared with (26).

Long flash. If $\alpha^2 \gg (Dt_0)^{-1}$ then

$$\begin{aligned} \Phi^{-1}(x_0) &\simeq \left[1 + \frac{\sqrt{\pi}}{2} x_0 \right]^{-1} \\ &\simeq \left(\frac{\sqrt{\pi}}{2} x_0 \right)^{-1} - \left(\frac{\sqrt{\pi}}{2} x_0 \right)^{-2} \end{aligned}$$

and (III,4) gives

c

$$U_s = \sqrt{\frac{4t_0}{\pi \kappa \sigma c}} \int E_0^\lambda d\lambda - \frac{4}{\pi \kappa} \int \alpha^{-1} E_0^\lambda d\lambda$$

The inert decay is given by

$$\begin{aligned} \sigma c \frac{dU}{dt} &= - \int \alpha E_0^\lambda (1 - Z_0(x_0)) d\lambda \\ &\approx - \int \alpha E_0^\lambda \left[1 - \frac{1}{\sqrt{\pi} x_0} \right] d\lambda \\ &= - \int \alpha E_0^\lambda d\lambda + \frac{\int E_0^\lambda d\lambda}{\sqrt{\pi \kappa t_0 \sigma c}} \\ &= - \int \alpha E_0^\lambda d\lambda \cdot \left[1 - \sqrt{\frac{\sigma c}{\pi \kappa t_0 \alpha^2}} \right] \\ &\approx - \int \alpha E_0^\lambda d\lambda \end{aligned}$$

since $\alpha^2 \gg (Dt_0)^{-1}$. Hence the analogue

of (21) is

$$\frac{d\theta}{dt} = - \frac{E}{RT_s^2} \frac{\int \alpha E_0^\lambda d\lambda}{\sigma c} + \frac{q \nu E}{c RT_s^2} \exp(-E/RT_s) e^\theta$$

which with the initial condition $\theta = 0$ when $t = 0$ gives

$$\eta = \omega + (1 - \omega) e^\chi$$

where

$$\chi = \frac{E}{RT_s^2} \frac{\int \alpha E_0^\lambda d\lambda}{\sigma c} \cdot t$$

and

$$\omega = \frac{q \sigma \nu \exp(-E/RT_s)}{\int \alpha E_0^\lambda d\lambda}$$

0

Explosion occurs if $\omega > 1$ (cf. (24)).

The critical condition may be written in the form

$$\frac{T_0}{T_A} + \frac{U_2}{T_A} = \left[\ln \left(\frac{q_{0v}}{\int \alpha E_0^\lambda d\lambda} \right) \right]^{-1}$$

or using (III,7),

$$E_{cr} \approx T_A K_1 \sqrt{\frac{\pi \kappa \sigma c t_0}{4}} \left[1 + \sqrt{\frac{4 \sigma c}{\pi \kappa t_0 \langle \alpha \rangle^2}} \right] \quad (\text{III,8})$$

where

$$K_1 = \left[\ln \left(\frac{q_{0v}}{\int \alpha E_0^\lambda d\lambda} \right) \right]^{-1} - \frac{T_0}{T_A}$$

and $\langle \alpha \rangle = \left\{ \overline{\alpha^{-1}} \right\}^{-1}$ is the harmonic mean

value of the absorption coefficient.

The use of this approximation

$$K_1 \approx \left[\ln \left(\frac{1}{\alpha_0^2 \bar{\alpha}^2} \right) \right]^{-1} - \frac{T_0}{T_A}$$

introduces only a small error into (III,8).

Thus (26) retains its validity provided the relevant average values $\hat{\alpha}$, $\bar{\alpha}$, $\langle \alpha \rangle$ of α are selected where

$$\bar{\alpha} = \int \alpha E_0^\lambda d\lambda / \int E_0^\lambda d\lambda ,$$

$$\hat{\alpha} = \int \alpha^2 E_0^\lambda d\lambda / \int \alpha E_0^\lambda d\lambda ,$$

$$\langle \alpha \rangle = \int E_0^\lambda d\lambda / \int \alpha^{-1} E_0^\lambda d\lambda .$$

If a more accurate approximation is required then the criteria $M_\alpha = 1$, $\omega_\alpha = 1$ should be used. In conclusion two important deductions can be made from this appendix.

- a) As the flash duration tends to zero the critical energy density for polychromatic light tends to the finite value

$$\mathcal{E}_{min} = \frac{\sigma c T_A}{\alpha} \left[\left\{ \ln \left(\frac{1}{\alpha_0^2 \alpha_1} \right) \right\}^{-1} - \frac{T_0}{T_A} \right]$$

- b) The critical energy of a polychromatic flash of "long" duration (i.e. for which $D t_0 \alpha^2 \gg 1$) is virtually independent of the absorption coefficient and has the approximate value

$$\mathcal{E}_\alpha = T_A \left(\frac{\pi \kappa \sigma c}{4} \right)^{\frac{1}{2}} \left[\left\{ \ln \left(\frac{1}{\alpha_0^2 \alpha_1} \right) \right\}^{-1} - \frac{T_0}{T_A} \right] t_0^{\frac{1}{2}}$$

i.e. is proportional to the square root of the flash duration.

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TABLE 1. THERMOCHEMICAL PARAMETERS OF SOME EXPLOSIVES

Substance	a_0 (Å)	$\sigma cT_A (10^4 \text{ cal cm}^{-3})$	$D (10^{-3} \text{ cm}^2 \text{ sec}^{-1})$
PETN	1.9×10^{-3}	1.41	1.02
RDX	3.6×10^{-3}	1.31	1.23
HMX	9.6×10^{-4}	1.46	1.27
Tetryl	2.0×10^{-1}	0.74	1.95
ACN_3	7.1×10^{-4}	1.25	1.49
PbN_6	2.5×10^{-1}	1.11	1.73

(Values calculated from data given in references^{1,20,21})

Fig.1.

The error function complement and related functions.

The n^{th} repeated integral $i^n \operatorname{erfc} z$ is
 labelled i^n , where $i^0 = \operatorname{erfc} z$. $Z_0(z)$ is the function
 $e^{z^2} \operatorname{erfc} z$. The function $\frac{2}{\sqrt{\pi}} e^{-z^2}$ is
 equivalent to $i^{-1} \operatorname{erfc} z$.

Ordinate: (not named)

Abscissa: z

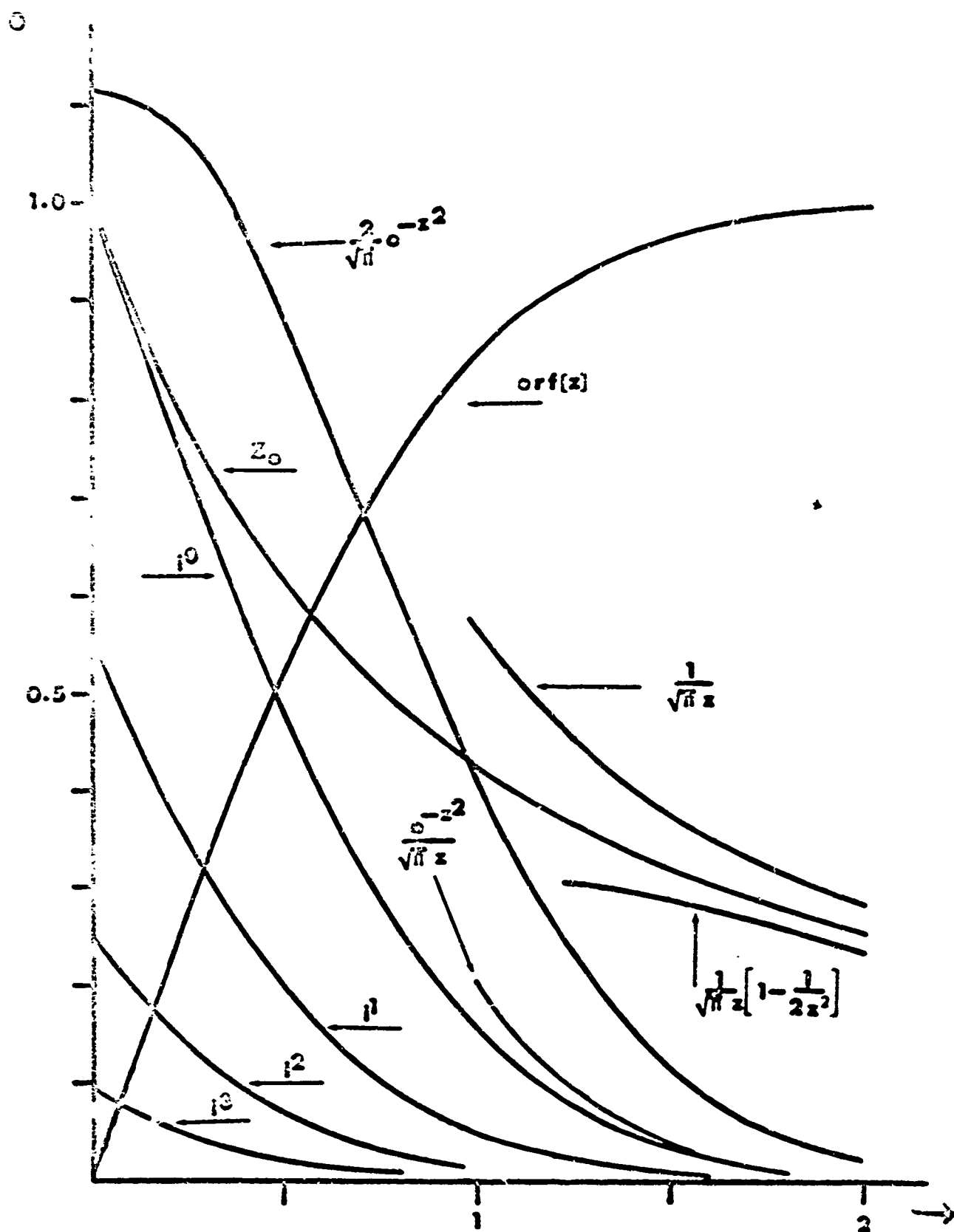


Fig 1

Fig. 2.

The temperature profiles produced by a rectangular flash of constant integrated intensity, \mathcal{E} , and of varying duration $\lambda^2 t_c$ according to equations (13' and (14). The area under each of the curves equals that enclosed by the dashed rectangle.

Ordinate:

$$U/\tau$$

Abscissa:

$$\rho$$

$$(\tau t_0)$$

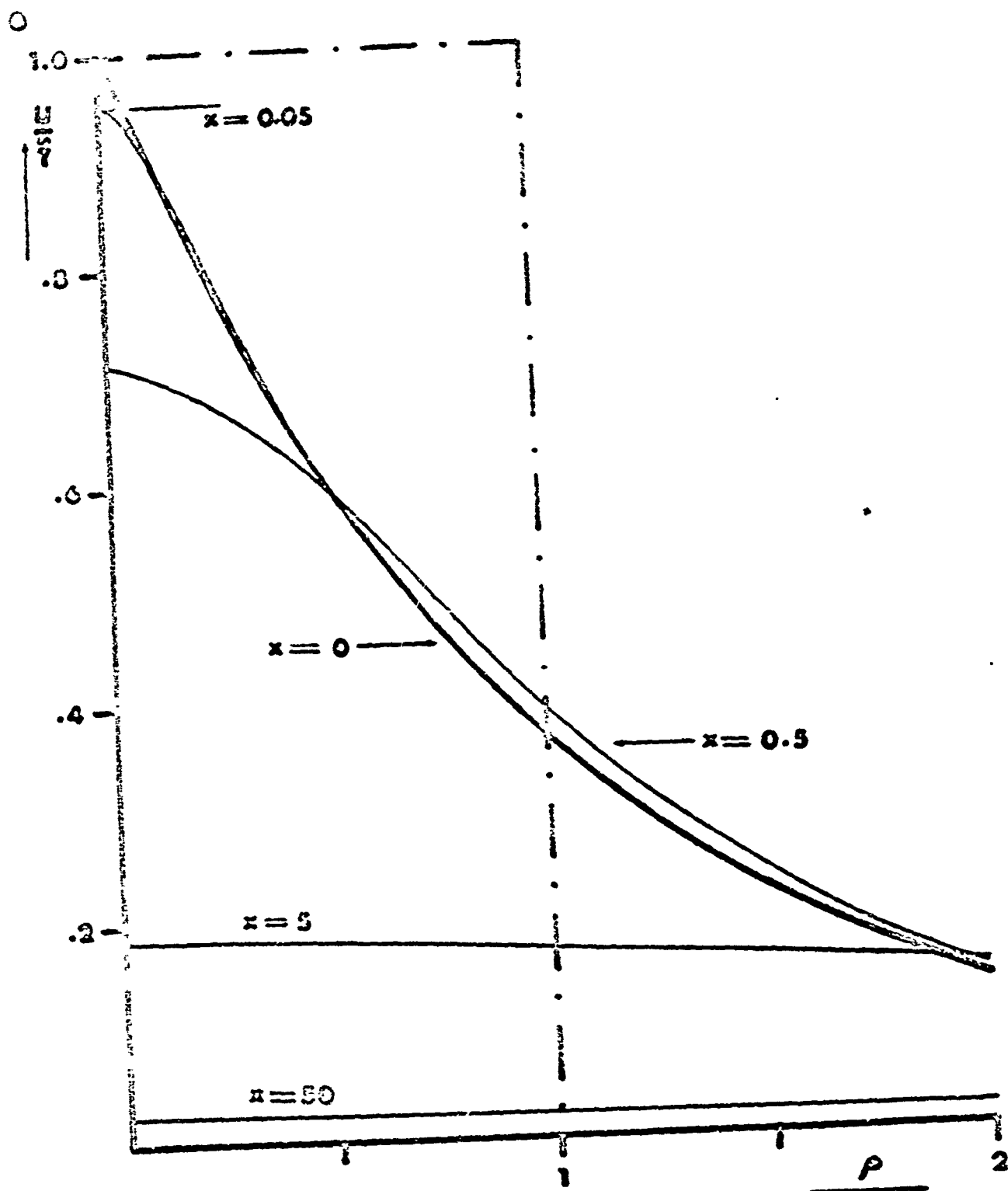


Fig 2

Fig. 3.

Evolution of the surface temperature after a short duration flash.

The curves belong to the family $\eta = \mu(1+y) + (1-\mu)e^y$.

The regime is critical (and fails to develop an explosion) when $\mu = 1$. The dashed curve gives the locus of the maxima in η (temperature minima) and is asymptotic to the line $\eta = y$ at large y .

Ordinate: $\eta = e^{-\delta}$

Abscissa: $y \quad \left\{ \propto t^{\frac{1}{2}} \right\}$

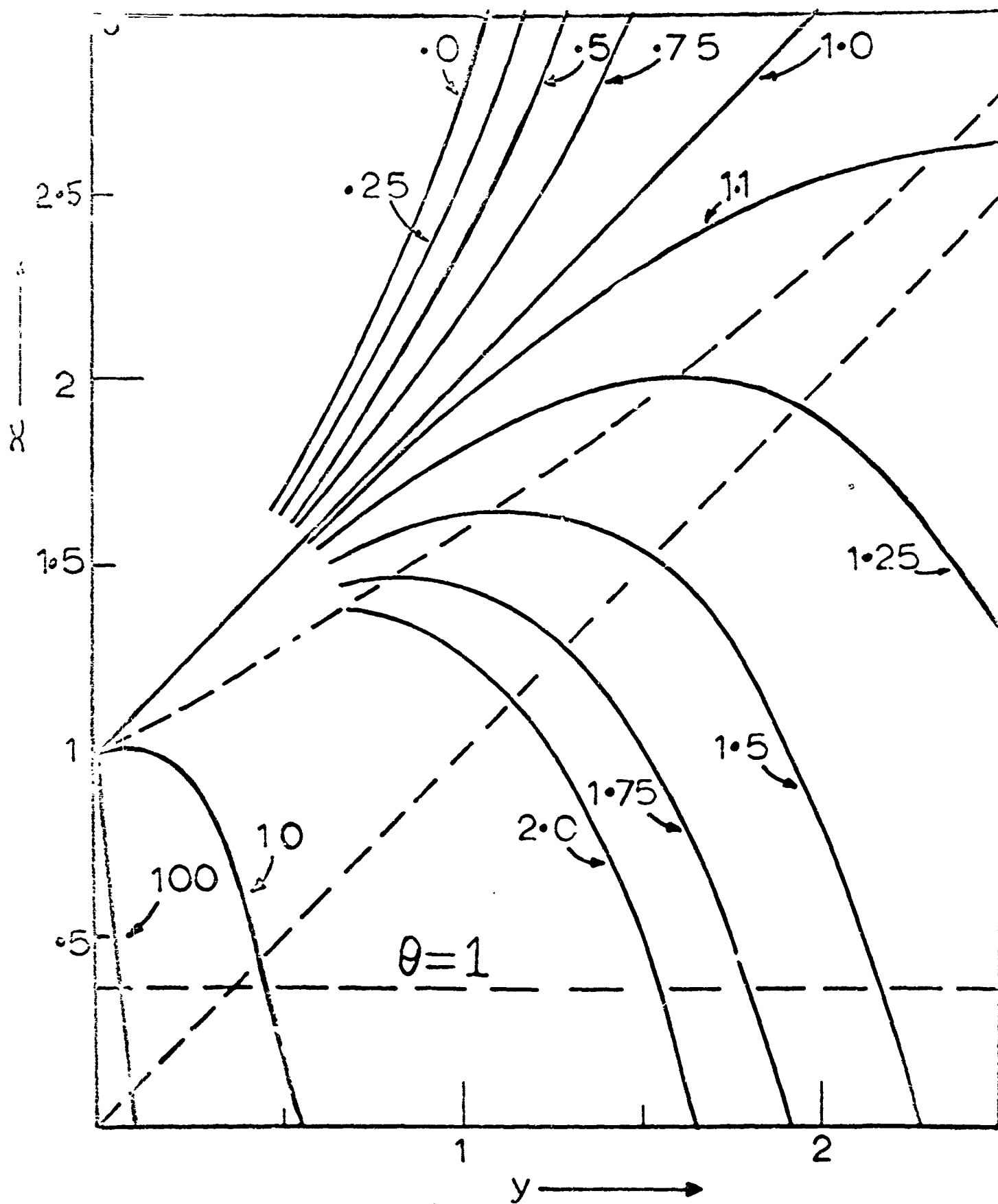


Fig 3

Fig. 4.

Evolution of the surface temperature
after a long duration flash.

The curves belong to the family :

$$\eta = \varepsilon + (1-\varepsilon) e^{C\tau} . \quad \text{The regime is critical (and fails to develop an explosion) when } \varepsilon = 1 .$$

Ordinate: $\eta = e^{-\delta}$

Abcissa: $C\tau \quad \{ \propto t \}$

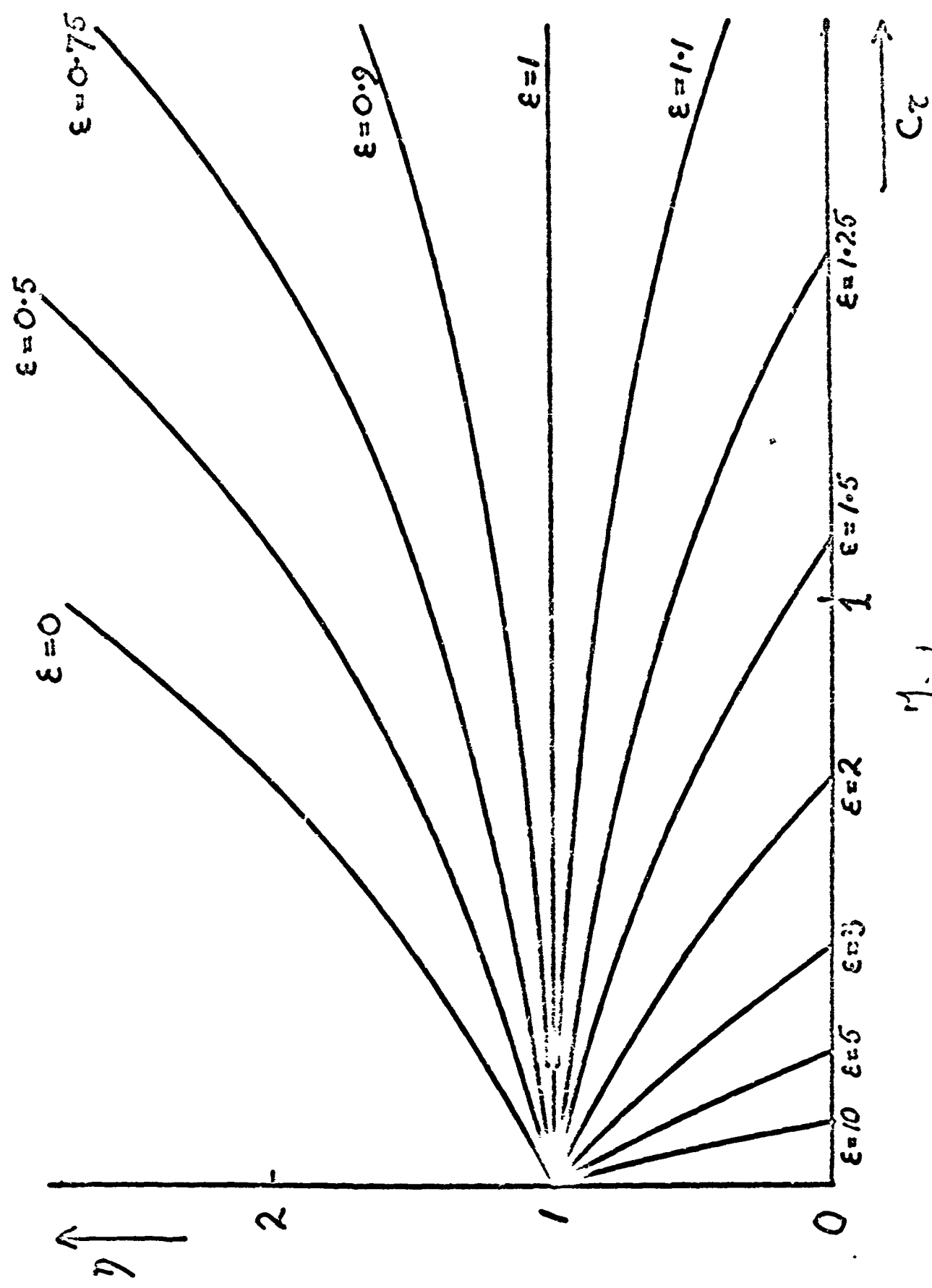


Fig 4

Fig. 5.

The function $\Phi(x) = x^2 \left\{ \frac{2x}{\sqrt{\pi}} + e^{x^2} \operatorname{erfc} x - 1 \right\}^{-1}$.

The lines A and B are the asymptotes of Φ for low and high values of x , respectively. The line E, which is parallel to B, represents the function used to estimate Φ for all values of x .

$\Phi(x_0)$ is approximately equal to the ratio $E_a(x_0) / E_{min}$.

Abscissa : x

Ordinate : (not named)

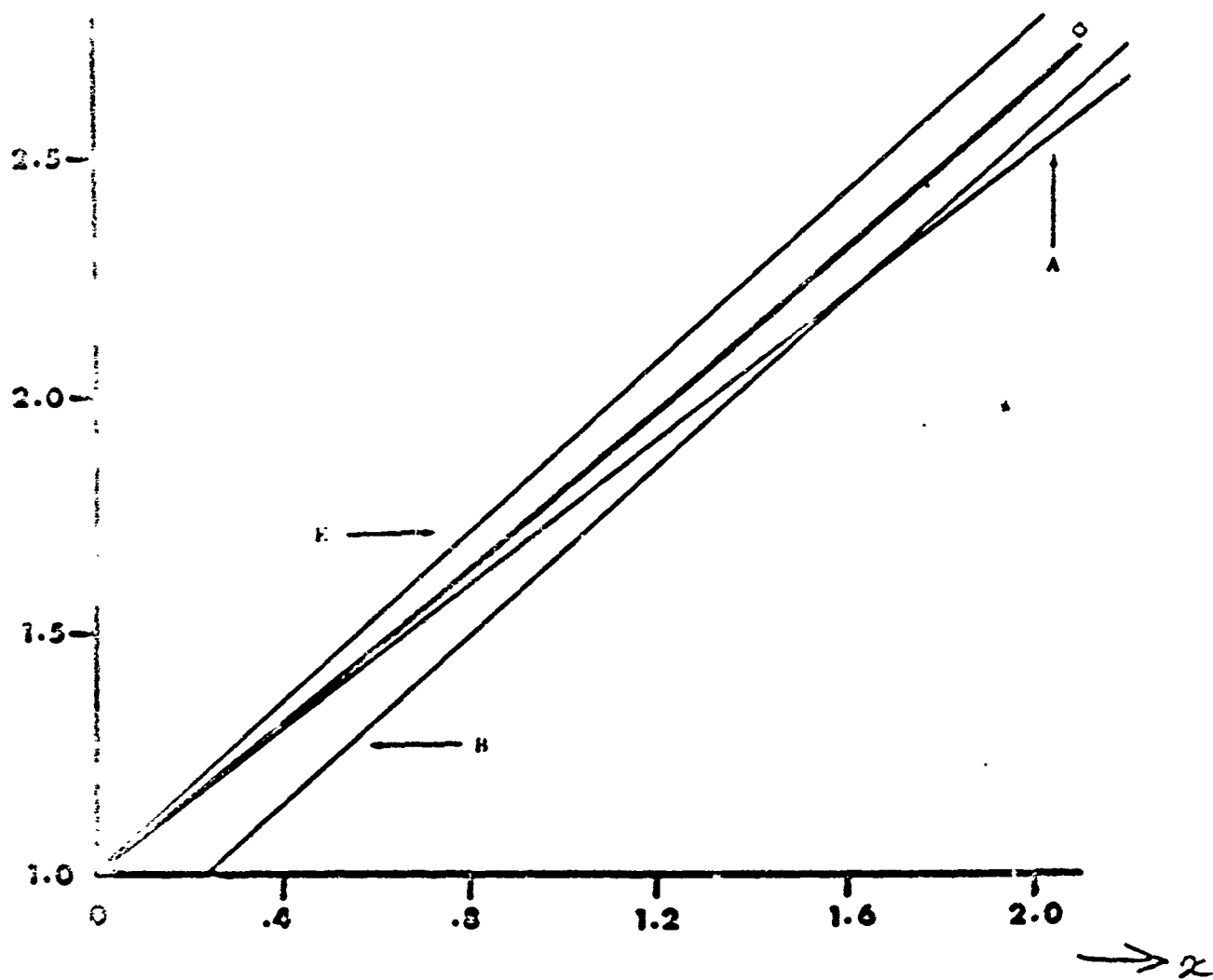


Fig 5

Fig. 6.

Variation of E_{cr} with the square root of time for Ag_3N calculated from Berchtold's data⁴. E_{cr} is in arbitrary units. a — best fit to the 4 points with high t_0 , b — best fit to all six points.

Ordinate: E_{cr} (arbitrary units)

Abcissa: $10^2 [t_0(\text{sec})]^{\frac{1}{2}}$

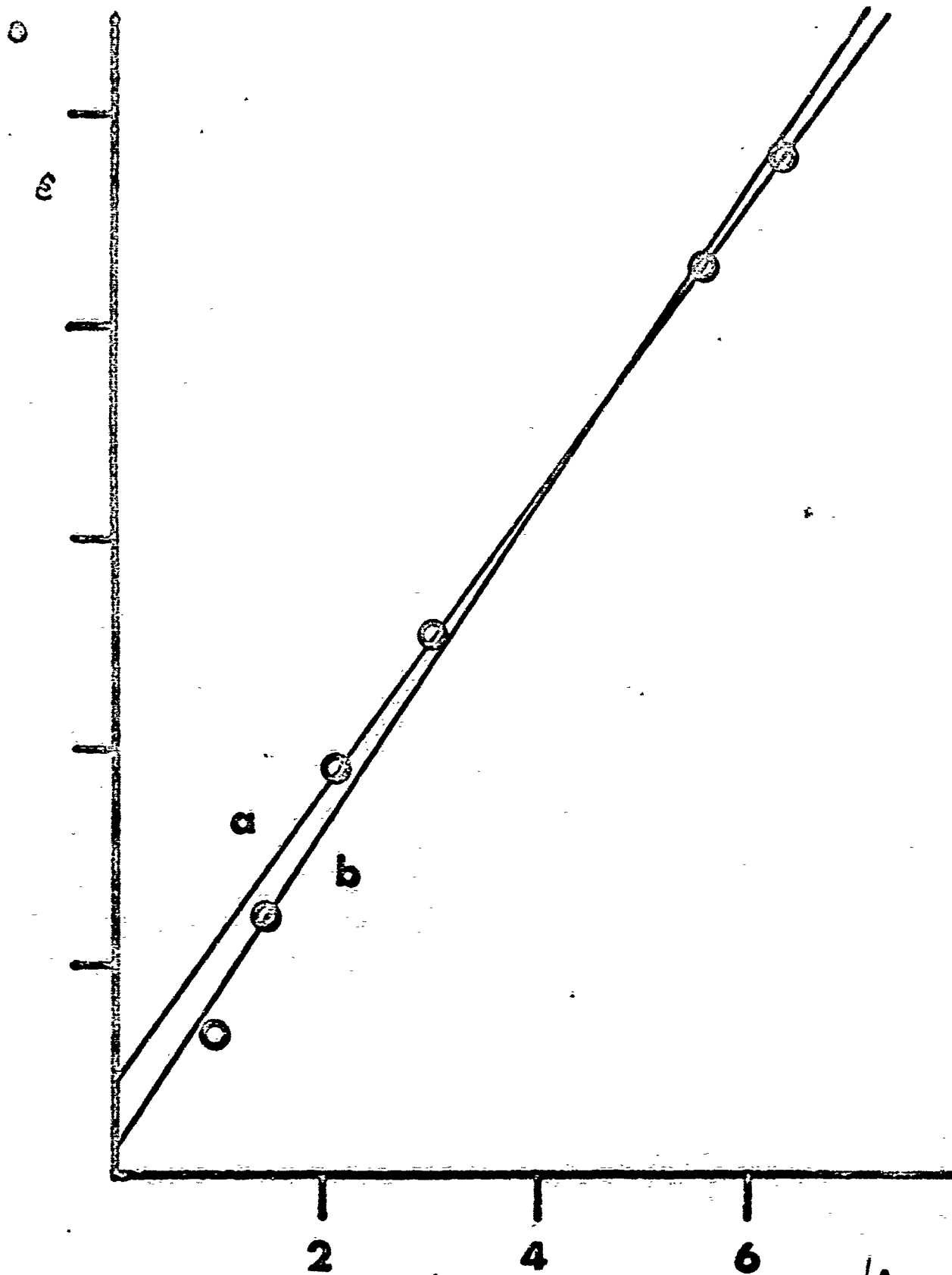


Fig 6

$v/80$

Fig. 7.

Variation of critical energy with ambient temperature
in the case of lead styphnate (after McAuslan^{1,16}).

- ★ - explosion
- - failure

Ordinate: Critical stored energy ($\frac{1}{2}CV^2$), Joules
Abscissa: Ambient temperature (°C)

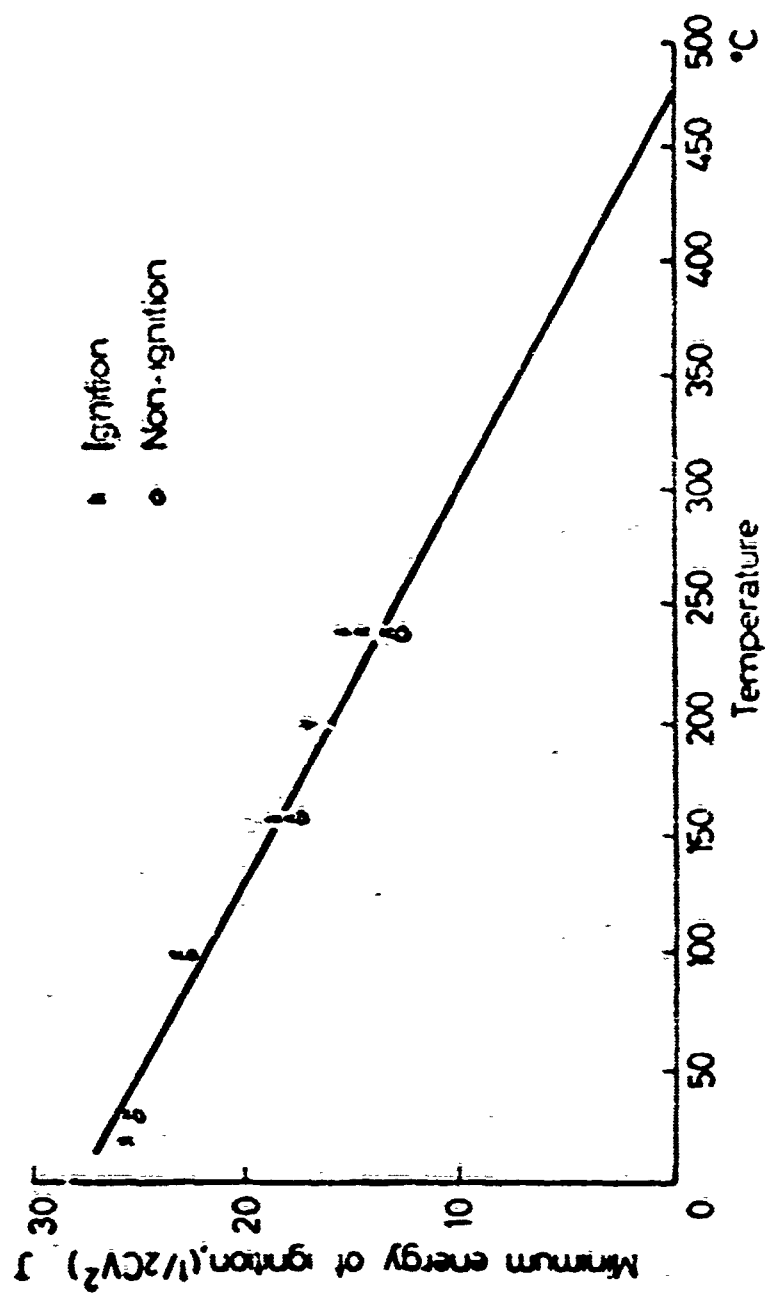


Fig 7

Fig. 8.

Evolution of surface temperature for the case of continuous intense irradiation with zero rise time. The curves are obtained by writing (II.3) in the form

$$\theta - \theta_0 = -\ln \left\{ -\psi + (1 + \psi) e^{-\Delta} \right\}$$

where $\Delta = B\tau$, $\psi = \frac{\int}{3\gamma_0}$, $B = \frac{A_0 E}{RT_0^2}$.

A critical profile is established in the conventional explosives somewhere between the two dashed lines. The present theory is invalid unless $\psi \lesssim 10^{-3}$.

Ordinate: $\theta - \theta_0$

Abscissa: Δ

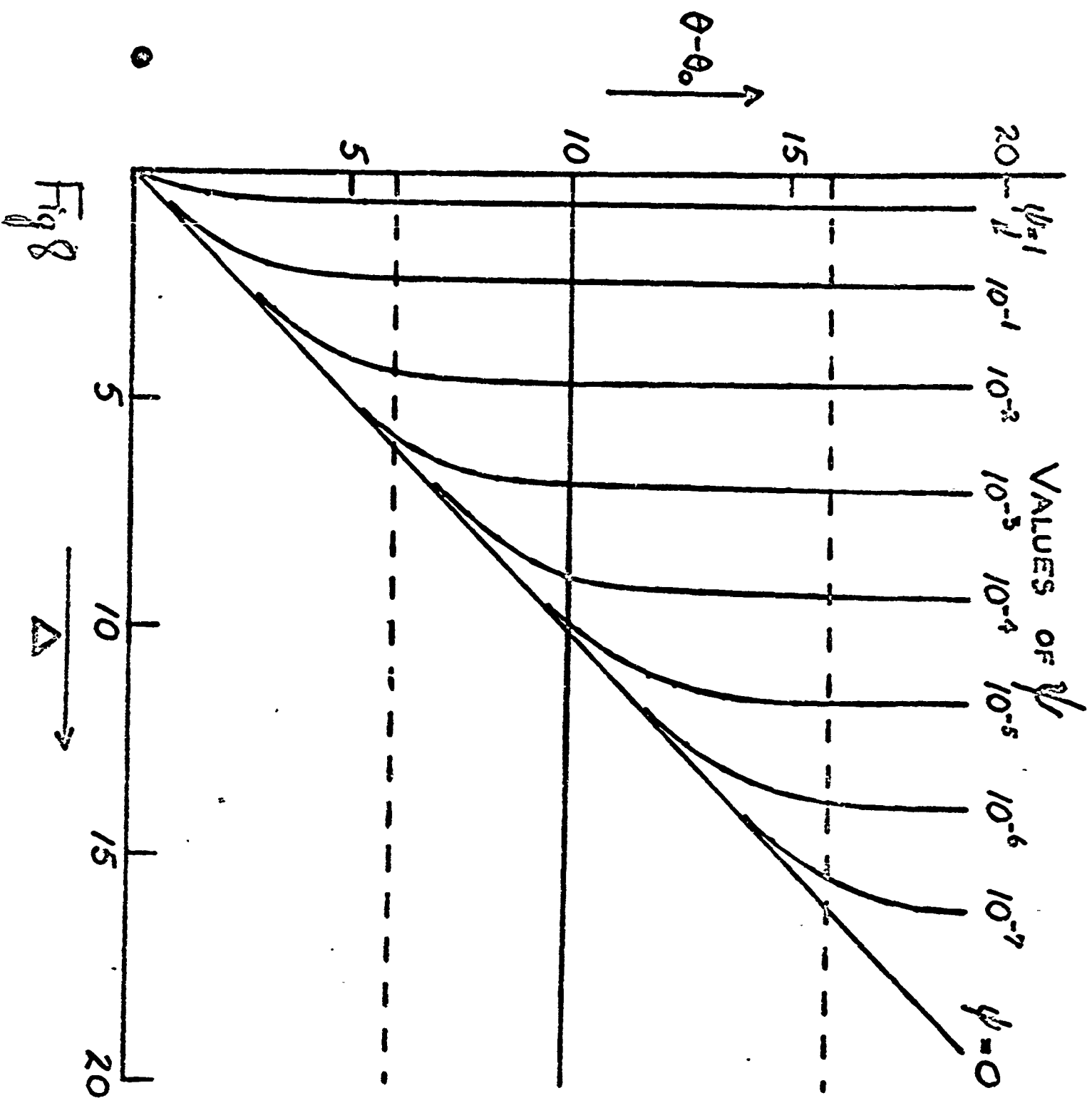


Fig 8